



# INFLUENCE OF AZOLE STABILIZERS ON AN ECOFRIENDLY ELECTROLESS COPPER NANO THIN FILM DEPOSITION

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## ABSTRACT

In this study the effects of azole stabilizers, viz., benzotriazole (BTA) and 2-Mercaptobenzothiazole (2-MBT) on electroless deposition of copper nano thin film from glycerol containing eco-friendly copper methanesulphonate bath were studied. Dimethylamineborane (DMAB) was used as reducing agent and potassium hydroxide (KOH) was used as pH adjuster. The electroless bath was optimized by addition of 1 ppm concentration of stabilizers at 13.0. Surface morphology and structural property of copper deposits were studied by atomic force microscopy (AFM) and x-ray diffraction (XRD) method. Electrochemical and corrosion kinetic properties were analyzed by cyclic voltammetry (CV). 2-Mercaptobenzothiazole was found to inhibit copper deposition while benzotriazole accelerated it. The crystallite size and surface roughness values were found to nano thin film deposition. Benzotriazole resulted in better physical and electrochemical properties of copper deposits than glycerol plain bath and 2-Mercaptobenzothiazole.

**KEYWORDS:** azole stabilizers, dimethylamineborane, glycerol, nano thin film, surface roughness.

## 1. Introduction

Electroless plating is an autocatalytic process more useful than electroplating for the deposition of metal coatings and films. It is purely chemical process and the coating is achieved through metal ion exchange using chemical reduction in solution (Schlesinger M., et al., 2000., Schlesinger M., et al., 2010). Electroless copper plating has found widespread acceptance in many applications such as in the fabrication of decorative articles, semiconductors, integrated circuits and through-hole plating in printed circuit boards.

Emerging applications of this technique lie in areas of electromagnetic interference shielding materials, ceramic or polymeric nanoparticles, aerospace, biomedical, automotive fields and energy conversion. Electroless plating of copper metal possesses advantages such as excellent solderability, possibility of plating even at room temperature and high conductivity than other metals (Ohno I., 1991).

These advantages and potential of electroless plating have resulted in considerable research being conducted in the field of nanochemistry in recent years (Balci S., et al., 2006., Rohan J F., et al., 2008., Chen-Yu Kao., et al., 2007., Huang Q., et al., 2000). Benzotriazole (BTA) is a well-known organic inhibitor in acidic medium. It contains a nitrogen-based polar group. These nitrogen atoms act as electron donors and enhance chemisorptions on the surface of the metal the vacant  $d$  orbital in copper atom form coordinate bonds with electron donating atoms such as nitrogen (Fox P G., et al., 1979., Kahled K F., 2009.). Additionally, there is also interaction with rings containing conjugation, and these result in corrosion inhibition (Antonijevic M M., et al., 2008).

BTA shows two polymeric structures, depending on the nature of the copper oxide present. BTA derivatives have been found to be good inhibitors in stimulated carbonation attack on concrete and afford protection to steel in SCP solution, indicating their applicability in reinforced concrete construction (Ababneh A., et al., 2009., Chadwick D., et al., 1978., Cho Sang Jin., et al., 2011., Kahled K F., et al., 2009). 2-MBT has been found to be the only inhibitor that provides effective protection to copper archaeological artifacts during preservation process (Schneble F.W., et al., 1966.).

In this work, a new bath based is studied wherein ecofriendly copper methanesulphonate is used instead of copper sulphate as the plating solution. BTA and 2-MBT as stabilizers in electroless copper deposition.

## 2. Materials and Methods:

The plating experiments were performed on an epoxy sheet (2.0 X 2.0 X 0.1 cm). The epoxy sheet was polished by grit paper and rinsed with double distilled water. A scoring process was used to clean the pre-cleaned substrate using KOH solution. After rinsing with distilled water, the substrate was surface etched using a solution of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  to remove any oxidized layer on the surface. In order to improve the deposition rate and adhesive properties of the Cu thin film, the surface was sensitized using  $\text{SnCl}_2$  solution ( $\text{SnCl}_2$  with  $\text{HCl}$ ) and activated using an  $\text{HCl}$  solution of  $\text{PdCl}_2$ . Table 1 shows that the bath composition carried out for electroless process.

**Table 1. Bath composition of copper methanesulphonate glycerol plain bath with stabilizers**

Bath contents	Plain bath	Stabilizers used bath
CuMS (II) ion contacting salt	3 g/L	3 g/L
Glycerol	20 ml/L	20 ml/L
Dimethylamineborane	10 g/L	10 g/L
KOH (pH )	13.0	13.0
Temperature	28±2 °C	28±2 °C
Stabilizers (BTA and 2-MBT)	0 ppm	1 ppm

## 2.1. Formula for rate and thickness of copper deposits

The rate of deposition (T) was calculated using the following relation

$$T = W \times 10^4 / dAt \quad [1]$$

Rate of the electroless copper deposit and thickness were calculated using the following equation

$$\text{Rate of deposition } (\mu\text{m/h}) = \text{Thickness} / \text{Deposition time} \quad [2]$$

$$\text{Thickness } (\mu\text{m}) = \frac{W \times 10^4 \times 60}{A \times D} \quad [3]$$

where,

$W = (w_1 - w_2)$  = Weight of deposit (g)

$w_1$  = Weight after plating (g)

$w_2$  = Weight after stripping (g)

A = Total plated area of the substrate ( $\text{cm}^2$ )

D = Density of the copper ( $\text{g/cm}^3$ )

## 3. Results and Discussion:

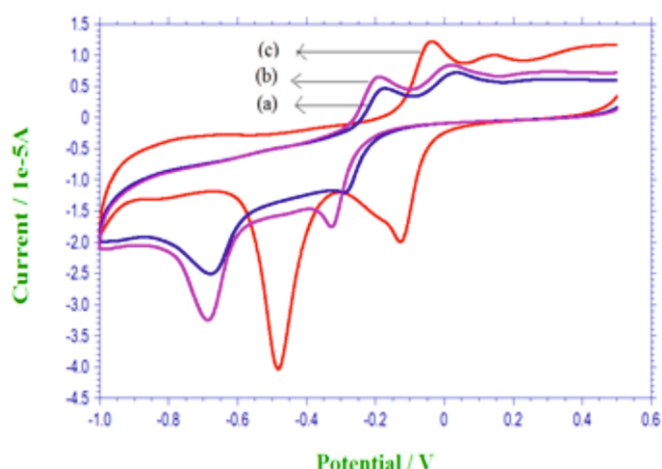
Glycerol containing methanesulphonate bath produced stable complexes with copper (II) ion in alkaline solutions. The plating process started at pH above 12 and optimum deposition rate was observed at pH 13, beyond which the deposition slowed down. In the absence of stabilizers, the rate of plating was poor. The effect of addition of small amount of stabilizers like 2-MBT, and BTA on the rate of deposition and bath stability were studied.

### 3.1. Electrochemical studies

Cyclic voltammetry was carried out to study the electrochemical properties of electroless copper solution and the role of the stabilizers. Cyclic voltammetric curves were obtained using standard electrochemical analyzer (CHI). The copper methanesulphonate solution was deaerated with nitrogen gas. The counter electrode was platinum wire and reference electrode was Ag/AgCl with saturated KCl solution.

The voltammograms were recorded at room temperature  $28 \pm 2^\circ\text{C}$  in 0.1 M  $\text{Na}_2\text{SO}_4$  as supporting electrolyte. Standard glassy carbon electrode was used as working electrode and the voltammograms were recorded in the range from -1.2 to +0.5 V at potential scanning rate  $50 \text{ Vs}^{-1}$ . The 0.1M  $\text{Na}_2\text{SO}_4$  supporting electrolyte solution was optimized by KOH solution pH 13 for glycerol baths. In Fig. 1, it is seen that the inhibiting and enhancing properties of stabilizers are confirmed by the anodic peak current value, anodic peak potential value and peak appearance.

Based on CV studies, the inhibiting properties of the stabilizer result in low anodic peak potential value. The low energy oxidation process is enhanced by the stabilizers. The appearances of the sharp peaks indicate that the rate of oxidation is high. The high anodic peak current value also indicates that the stabilizer inhibits the deposition of copper. The low anodic peak current, high peak potential and broad peaks indicate the enhancing properties of the stabilizers.



**Figure 1.** Cyclic voltammogram for electroless copper methanesulphonate glycerol bath at pH 13.0; (a) 2-MBT bath, (b) glycerol plain bath and (c) BTA bath.

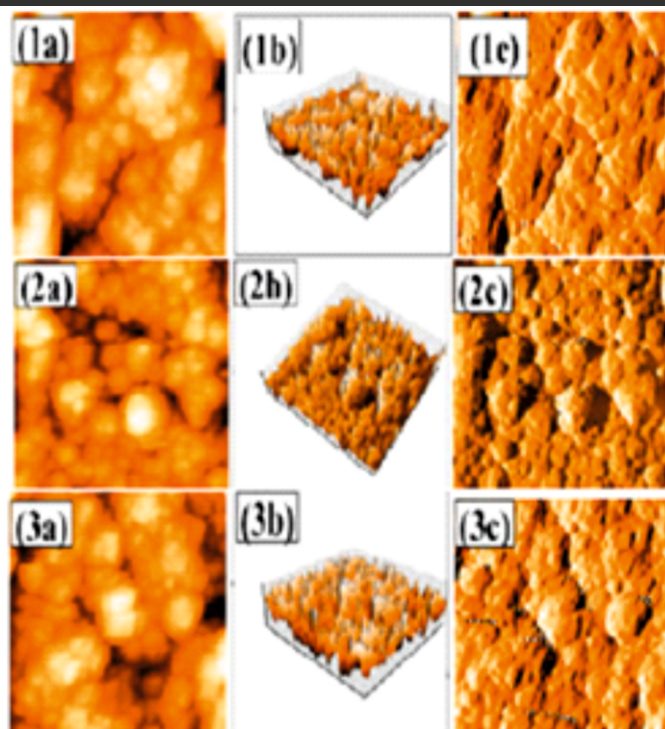
### 3.2. Atomic Force Microscope (AFM)

Bright copper deposits seen in atomic force microscopy (AFM) indicate better mechanical and physical properties. Roughness values are inversely proportional to smooth deposition. Table 2 and Fig. 2 indicate the roughness values of the glycerol plain bath and bath with the two stabilizers.

**Table 2.** Influence of various physical and surface morphologies of glycerol plain bath with azole stabilizers (1 ppm) on electroless copper bath.

Surface morphologies	Glycerol Plain bath	Stabilizers used glycerol baths	
		2-MBT	BTA
Crystallite size (nm)	126	132	98
Deposition rate ( $\mu\text{m/h}$ )	3.02	2.68	3.16
Epa-1 (mV)	-0.2168	-0.2380	-0.2120
Roughness value (nm)	208	92	68
Thickness ( $\mu\text{m}$ )	181.2	160.8	189.6

The glycerol plain bath produced maximum roughness value of 208 nm. On using stabilizers, the roughness values decreased and observed at 92 nm for 2-MBT and 68 nm for BTA. Because of steric factors conjugation effect and presence of hetero atoms significantly influence the surface morphologies.

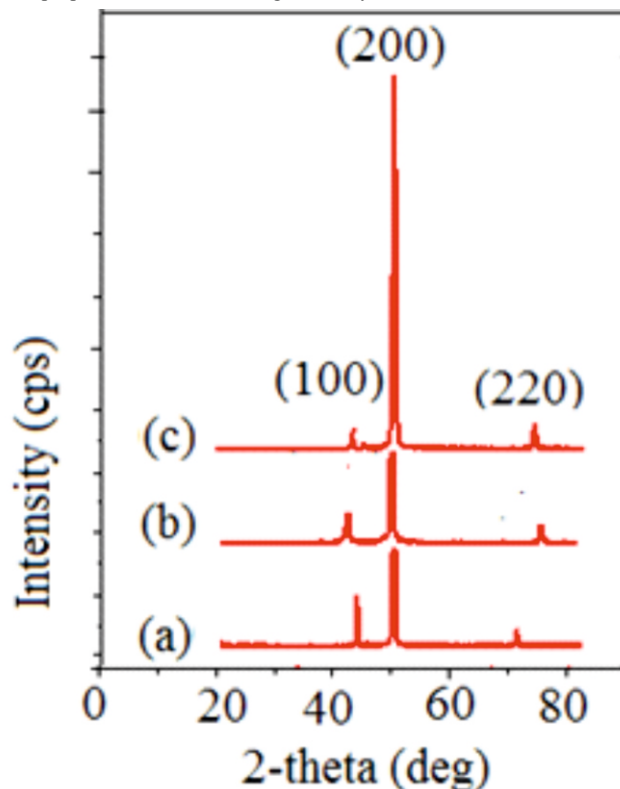


**Figure 2.** AFM images of copper deposits on methanesulphonate glycerol plain bath (a) topography of copper deposits (b) 3-D image and (c) surface area.

### 3.3. X-ray Diffraction (XRD)

The crystal orientations and lattice parameters were studied by XRD. Copper methanesulphonate bath results in large quantities of copper ions, because of high conductivity and solubility leading to (200) plane. Fig.3. shows that the crystallite size of the copper deposits can be estimated by using Debye Scherrer's equation (Debye P., 1916).

Where K is the Scherrer constant, ' $\lambda$ ' is the wavelength of light used for the diffraction, ' $\beta$ ' is the 'Full Width at Half Maximum' of the sharp peaks and ' $\theta$ ' is the angle measured. The Scherrer constant (K) in the above formula accounts for the shape of the particle and is generally taken to have the value 0.89. Crystallite sizes are proportional to the inhibiting efficiency.



**Figure 3.** XRD pattern of copper deposits on methanesulphonate glycerol plain bath with azole derivatives stabilizers (1 ppm); (a) 2-MBT bath (b) glycerol plain bath, (c) BTA.

**4. Conclusion:**

The autocatalytic reduction of Cu (II) by formaldehyde from a solution of glycerol containing copper methanesulphonate ligand starts at pH above 12, reaches optimization at pH 13, the bath decreases the plating rate and extends the bath life time. AFM studies of the deposits formed in 2-MBT containing bath show the deposits to be dark brown in color. The copper deposits from BTA containing bath are brighter and of smaller grain sizes. XRD studies validate crystallite size of the copper deposits in all cases. The deposits are found to have higher (200) plane orientation. Benzotriazole containing bath produces bright deposits with, uniform, compact and fine structure.

**REFERENCES:**

1. Ababneh, A., Sheban, M., Abu-Dalo, M., and Andreescu S. (2009). 'Effect of benzotriazole derivatives on steel corrosion in solution simulated carbonated concrete'. Jordan journal of civil engineering, Vol. 3, pp. 91-102.
2. Antonijevic, M M. and Petrovic, M B. (2008). 'Copper Corrosion Inhibitors. A review', Int. J. Electrochem. Sci, Vol. 3, pp.1-28.
3. Balci, S., Bittner, A M., Hahn, K., Scheu, C., Knez, M., Kadri, A., Wege, C., Jeske, H. and Kern, K. (2006). *ElectrochimicaActa*, 51, 6251-6257.
4. Chadwick, D. and Hashemi, T. (1978). 'Adsorbed corrosion inhibitors studied by electron spectroscopy: Benzotriazole on copper and copper alloys'. *Corrosion Science*, Vol.18, pp. 39-51.
5. Chen-Yu Kao. and Kan-Sen Chou. (2007). 'Electroless copper plating onto printed lines of nanosized silver seeds electrochem'. *Solid-State Lett*, Vol. 10, pp.D32-D34.
6. Cho Sang Jin., Nguyen Trieu. and Boo Jin Hyo. (2011). 'Polyimide surface modification by using microwave plasma for adhesion enhancement of copper electroless plating'. *Journal of nanoscience and nanotechnology*, Vol.11, pp. 5328-5333.
7. Debye, P. and Scherrer, P. (1916). 'Interference of irregularly oriented particles in x-rays'. *Phys. Ziet*, Vol. 17, pp.277-283.
8. Fox, P G., Lewis, G. and Boden, P J. (1979). 'Some chemical aspects of the corrosion inhibition of copper by benzotriazole'. *Corrosion Science*., Vol.19, pp. 457-467.
9. Huang, Q., Gu, M Y. and Jin, Y P. (2000). 'Electronic packaging materials research. *Materials Review*., Vol. 114, pp. 28-30.
10. Kahled, K F. (2009). 'Experimental and atomistic simulation studies of corrosion inhibition of copper by a new benzotriazole derivative in acid medium'.*ElectrochimicaActa*., Vol. 54, pp. 4345-4352.
11. Khaled, K F., Fadl Allah, S A. and Hammouti, B. (2009). 'Some benzotriazole derivatives as corrosion inhibitors for copper in acidic medium: Experimental and quantum chemical molecular dynamics approach'. *Mat., Chem., and Phys.*, Vol. 117, pp. 148-155.
12. Ohno, I. (1991). 'Electrochemistry of electroless plating'. *J. Mat. Sci. Eng.*, Vol. 146, pp. 33-49.
13. Rohan, J F., Casey, D P., Ahern, B M., Rhen, F M F., Roy, S., Fleming, D., and Lawrence, S E. (2008). 'Electrochem. Commun, 10, 1419-1422.
14. Schlesinger, M. and Paunovic, M. (2000). 'Modern electroplating'. 4th edition, New York, John Wiley, Vol. 14, pp. 868.
15. Schlesinger, M., (Editor). and Paunovic, M., (Editor). (2010). 'Modern Electroplating'. 5th Edition, New York, John Wiley, pp. 736.
16. Schneble, F W. and Zeblicky, R J. (1966). U.S.Patent. 3,257,215.